

Figure 2. Schematic diagram of a typical calibration apparatus using an NO<sub>2</sub> permeation device.

[41 FR 52688, Dec. 1, 1976, as amended at 48 FR 2529, Jan 20, 1983]

# APPENDIX G TO PART 50—REFERENCE METHOD FOR THE DETERMINATION OF LEAD IN SUSPENDED PARTICULATE MATTER COLLECTED FROM AMBIENT AIR

## 1. Principle and applicability.

1.1 Ambient air suspended particulate matter is collected on a glass-fiber filter for 24 hours using a high volume air sampler. The analysis of the 24-hour samples may be performed for either individual samples or composites of the samples collected over a calendar month or quarter, provided that the compositing procedure has been approved in accordance with section 2.8 of Appendix C to Part 58 of this chapter—*Modifications of methods by users*. (Guidance or assistance in requesting approval under Section 2.8 can be obtained from the address given in section 2.7 of Appendix C to Part 58 of this chapter.)

1.2 Lead in the particulate matter is solubilized by extraction with nitric acid (HNO<sub>3</sub>), facilitated by heat or by a mixture of HNO<sub>3</sub> and hydrochloric acid (HCl) facilitated by ultrasonication.

1.3 The lead content of the sample is analyzed by atomic absorption spectrometry using an air-acetylene flame, the 283.3 or 217.0 nm lead absorption line, and the optimum instrumental conditions recommended by the manufacturer.

1.4 The ultrasonication extraction with HNO<sub>3</sub>/HCl will extract metals other than lead from ambient particulate matter.

2. *Range, sensitivity, and lower detectable limit.* The values given below are typical of the methods capabilities. Absolute values will vary for individual situations depending on the type of instrument used, the lead line, and operating conditions.

2.1 *Range.* The typical range of the method is 0.07 to 7.5 µg Pb/m<sup>3</sup> assuming an upper linear range of analysis of 15 µg/ml and an air volume of 2,400 m<sup>3</sup>.

2.2 *Sensitivity.* Typical sensitivities for a 1 percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 µg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 *Lower detectable limit (LDL).* A typical LDL is 0.07 µg Pb/m<sup>3</sup>. The above value was calculated by doubling the between-laboratory standard deviation obtained for the lowest measurable lead concentration in a collaborative test of the method.<sup>(15)</sup> An air volume of 2,400 m<sup>3</sup> was assumed.

3. *Interferences.* Two types of interferences are possible: chemical and light scattering.

3.1 *Chemical.* Reports on the absence (1, 2, 3, 4, 5) of chemical interferences far outweigh those reporting their presence. (6) therefore, no correction for chemical interferences is given here. If the analyst suspects that the sample matrix is causing a

chemical interference, the interference can be verified and corrected for by carrying out the analysis with and without the method of standard additions.(7)

3.2 *Light scattering.* Nonatomic absorption or light scattering, produced by high concentrations of dissolved solids in the sample, can produce a significant interference, especially at low lead concentrations. (2) The interference is greater at the 217.0 nm line than at the 283.3 nm line. No interference was observed using the 283.3 nm line with a similar method.(1)

Light scattering interferences can, however, be corrected for instrumentally. Since the dissolved solids can vary depending on the origin of the sample, the correction may be necessary, especially when using the 217.0 nm line. Dual beam instruments with a continuum source give the most accurate correction. A less accurate correction can be obtained by using a nonabsorbing lead line that is near the lead analytical line. Information on use of these correction techniques can be obtained from instrument manufacturers' manuals.

If instrumental correction is not feasible, the interference can be eliminated by use of the ammonium pyrrolidinedithioate-methylisobutyl ketone, chelation-solvent extraction technique of sample preparation.(8)

#### 4. Precision and bias.

4.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7 percent over the range 80 to 125  $\mu\text{g}/\text{m}^3$ .(9) The combined extraction-analysis procedure has an average within-laboratory relative standard deviation of 5 to 6 percent over the range 1.5 to 15  $\mu\text{g}$  Pb/ml, and an average between laboratory relative standard deviation of 7 to 9 percent over the same range. These values include use of either extraction procedure.

4.2 Single laboratory experiments and collaborative testing indicate that there is no significant difference in lead recovery between the hot and ultrasonic extraction procedures.(15)

#### 5. Apparatus.

##### 5.1 Sampling.

5.1.1 *High-Volume Sampler.* Use and calibrate the sampler as described in Appendix B to this part.

##### 5.2 Analysis.

5.2.1 *Atomic absorption spectrophotometer.* Equipped with lead hollow cathode or electrodeless discharge lamp.

5.2.1.1 *Acetylene.* The grade recommended by the instrument manufacturer should be used. Change cylinder when pressure drops below 50-100 psig.

5.2.1.2 *Air.* Filtered to remove particulate, oil, and water.

5.2.2 *Glassware.* Class A borosilicate glassware should be used throughout the analysis.

5.2.2.1 *Beakers.* 30 and 150 ml. graduated, Pyrex.

5.2.2.2 *Volumetric flasks.* 100-ml.

5.2.2.3 *Pipettes.* To deliver 50, 30, 15, 8, 4, 2, 1 ml.

5.2.2.4 *Cleaning.* All glassware should be scrupulously cleaned. The following procedure is suggested: Wash with laboratory detergent, rinse, soak for 4 hours in 20 percent (w/w)  $\text{HNO}_3$ , rinse 3 times with distilled-deionized water, and dry in a dust free manner.

5.2.3 *Hot plate.*

5.2.4 *Ultrasonication water bath, unheated.* Commercially available laboratory ultrasonic cleaning baths of 450 watts or higher "cleaning power," i.e., actual ultrasonic power output to the bath have been found satisfactory.

5.2.5 *Template.* To aid in sectioning the glass-fiber filter. See figure 1 for dimensions.

5.2.6 *Pizza cutter.* Thin wheel. Thickness 1mm.

5.2.7 *Watch glass.*

5.2.8 *Polyethylene bottles.* For storage of samples. Linear polyethylene gives better storage stability than other polyethylenes and is preferred.

5.2.9 *Parafilm "M".*<sup>1</sup> American Can Co., Marathon Products, Neenah, Wis., or equivalent.

#### 6. Reagents.

##### 6.1 Sampling.

6.1.1 *Glass fiber filters.* The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties. These specifications have been met by EPA contractors.

6.1.1.1 *Lead content.* The absolute lead content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a lead content of 75  $\mu\text{g}/\text{filter}$ .

It is important that the variation in lead content from filter to filter, within a given batch, be small.

##### 6.1.1.2 Testing.

6.1.1.2.1 For large batches of filters (>500 filters) select at random 20 to 30 filters from a given batch. For small batches (>500 filters) a lesser number of filters may be taken. Cut one  $\frac{1}{4}$ "x8" strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

6.1.1.2.2 Calculate the total lead in each filter as

<sup>1</sup> Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

$$F_b = \mu\text{g Pb/ml} \times \frac{100\text{ml}}{\text{strip}} \times \frac{12\text{strips}}{\text{filter}}$$

where:

$F_b$  = Amount of lead per 72 square inches of filter,  $\mu\text{g}$ .

$$y = \frac{77\text{ml} \times 0.15 \times}{0.9M}$$

where:

$y$  = ml of concentrated HCl required.

$x$  = molarity of HCl in 6.2.6.

0.15 = dilution factor in 7.2.2.

6.1.1.2.3 Calculate the mean,  $F_b$ , of the values and the relative standard deviation (standard deviation/mean  $\times$  100). If the relative standard deviation is high enough so that, in the analysts opinion, subtraction of  $F_b$  (section 10.3) may result in a significant error in the  $\mu\text{g Pb/m}^2$  the batch should be rejected.

6.1.1.2.4 For acceptable batches, use the value of  $F_b$  to correct all lead analyses (section 10.3) of particulate matter collected using that batch of filters. If the analyses are below the LDL (section 2.3) no correction is necessary.

#### 6.2 Analysis.

6.2.1 Concentrated (15.6 M)  $\text{HNO}_3$ . ACS reagent grade  $\text{HNO}_3$  and commercially available redistilled  $\text{HNO}_3$  has found to have sufficiently low lead concentrations.

6.2.2 Concentrated (11.7 M) HCl. ACS reagent grade.

6.2.3 Distilled-deionized water. (D.I. water).

6.2.4 3 M  $\text{HNO}_3$ . This solution is used in the hot extraction procedure. To prepare, add 192 ml of concentrated  $\text{HNO}_3$  to D.I. water in a 1 l volumetric flask. Shake well, cool, and dilute to volume with D.I. water. **Caution:** Nitric acid fumes are toxic. Prepare in a well ventilated fume hood.

6.2.5 0.45 M  $\text{HNO}_3$ . This solution is used as the matrix for calibration standards when using the hot extraction procedure. To prepare, add 29 ml of concentrated  $\text{HNO}_3$  to D.I. water in a 1 l volumetric flask. Shake well, cool, and dilute to volume with D.I. water.

6.2.6 2.6 M  $\text{HNO}_3$  + 0 to 0.9 M HCl. This solution is used in the ultrasonic extraction procedure. The concentration of HCl can be varied from 0 to 0.9 M. Directions are given for preparation of a 2.6 M  $\text{HNO}_3$  + 0.9 M HCl solution. Place 167 ml of concentrated  $\text{HNO}_3$  into a 1 l volumetric flask and add 77 ml of concentrated HCl. Stir 4 to 6 hours, dilute to nearly 1 l with D.I. water, cool to room temperature, and dilute to 1 l.

6.2.7 0.40 M  $\text{HNO}_3$  + X M HCl. This solution is used as the matrix for calibration standards when using the ultrasonic extraction procedure. To prepare, add 26 ml of concentrated  $\text{HNO}_3$  plus the ml of HCl required, to a 1 l volumetric flask. Dilute to nearly 1 l with D.I. water, cool to room temperature, and dilute to 1 l. The amount of HCl required can be determined from the following equation:

6.2.8 Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ . ACS reagent grade, purity 99.0 percent. Heat for 4 hours at 120° C and cool in a desiccator.

#### 6.3 Calibration standards.

6.3.1 Master standard, 1000  $\mu\text{g Pb/ml}$  in  $\text{HNO}_3$ . Dissolve 1.598 g of  $\text{Pb}(\text{NO}_3)_2$  in 0.45 M  $\text{HNO}_3$ , contained in a 1 l volumetric flask and dilute to volume with 0.45 M  $\text{HNO}_3$ .

6.3.2 Master standard, 1000  $\mu\text{g Pb/ml}$  in  $\text{HNO}_3/\text{HCl}$ . Prepare as in section 6.3.1 except use the  $\text{HNO}_3/\text{HCl}$  solution in section 6.2.7.

Store standards in a polyethylene bottle. Commercially available certified lead standard solutions may also be used.

#### 7. Procedure.

7.1 Sampling. Collect samples for 24 hours using the procedure described in reference 10 with glass-fiber filters meeting the specifications in section 6.1.1. Transport collected samples to the laboratory taking care to minimize contamination and loss of sample. (16).

#### 7.2 Sample preparation.

##### 7.2.1 Hot extraction procedure.

7.2.1.1 Cut a  $\frac{1}{4}$ "  $\times$  8" strip from the exposed filter using a template and a pizza cutter as described in Figures 1 and 2. Other cutting procedures may be used.

Lead in ambient particulate matter collected on glass fiber filters has been shown to be uniformly distributed across the filter. "Another study" has shown that when sampling near a roadway, strip position contributes significantly to the overall variability associated with lead analyses. Therefore, when sampling near a roadway, additional strips should be analyzed to minimize this variability.

7.2.1.2 Fold the strip in half twice and place in a 150-ml beaker. Add 15 ml of 3 M  $\text{HNO}_3$  to cover the sample. The acid should completely cover the sample. Cover the beaker with a watch glass.

7.2.1.3 Place beaker on the hot-plate, contained in a fume hood, and boil gently for 30 min. Do not let the sample evaporate to dryness. **Caution:** Nitric acid fumes are toxic.

7.2.1.4 Remove beaker from hot plate and cool to near room temperature.

7.2.1.5 Quantitatively transfer the sample as follows:

7.2.1.5.1 Rinse watch glass and sides of beaker with D.I. water.

7.2.1.5.2 Decant extract and rinsings into a 100-ml volumetric flask.

7.2.1.5.3 Add D.I. water to 40 ml mark on beaker, cover with watch glass, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted since it allows the  $\text{HNO}_3$ , trapped in the filter to diffuse into the rinse water.

7.2.1.5.4 Decant the water from the filter into the volumetric flask.

7.2.1.5.5 Rinse filter and beaker twice with D.I. water and add rinsings to volumetric flask until total volume is 80 to 85 ml.

7.2.1.5.6 Stopper flask and shake vigorously. Set aside for approximately 5 minutes or until foam has dissipated.

7.2.1.5.7 Bring solution to volume with D.I. water. Mix thoroughly.

7.2.1.5.8 Allow solution to settle for one hour before proceeding with analysis.

7.2.1.5.9 If sample is to be stored for subsequent analysis, transfer to a linear polyethylene bottle.

## 7.2.2 Ultrasonic extraction procedure.

7.2.2.1 Cut a  $\frac{1}{4}$ " x 8" strip from the exposed filter as described in section 7.2.1.1.

7.2.2.2 Fold the strip in half twice and place in a 30 ml beaker. Add 15 ml of the  $\text{HNO}_3/\text{HCl}$  solution in section 6.2.6. The acid should completely cover the sample. Cover the beaker with parafilm.

The parafilm should be placed over the beaker such that none of the parafilm is in contact with water in the ultrasonic bath. Otherwise, rinsing of the parafilm (section 7.2.2.4.1) may contaminate the sample.

7.2.2.3 Place the beaker in the ultrasonic bath and operate for 30 minutes.

7.2.2.4 Quantitatively transfer the sample as follows:

7.2.2.4.1 Rinse parafilm and sides of beaker with D.I. water.

7.2.2.4.2 Decant extract and rinsings into a 100 ml volumetric flask.

7.2.2.4.3 Add 20 ml D.I. water to cover the filter strip, cover with parafilm, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted. The sample is then processed as in sections 7.2.1.5.4 through 7.2.1.5.9.

NOTE: Samples prepared by the hot extraction procedure are now in 0.45 M  $\text{HNO}_3$ . Samples prepared by the ultrasonication procedure are in 0.40 M  $\text{HNO}_3$  + X M  $\text{HCl}$ .

## 8. Analysis.

8.1 Set the wavelength of the monochromator at 283.3 or 217.0 nm. Set or align other instrumental operating conditions as recommended by the manufacturer.

8.2 The sample can be analyzed directly from the volumetric flask, or an appropriate amount of sample decanted into a sample analysis tube. In either case, care should be taken not to disturb the settled solids.

8.3 Aspirate samples, calibration standards and blanks (section 9.2) into the flame and record the equilibrium absorbance.

8.4 Determine the lead concentration in  $\mu\text{g Pb/ml}$ , from the calibration curve, section 9.3.

8.5 Samples that exceed the linear calibration range should be diluted with acid of the same concentration as the calibration standards and reanalyzed.

## 9. Calibration.

9.1 Working standard, 20  $\mu\text{g Pb/ml}$ . Prepared by diluting 2.0 ml of the master standard (section 6.3.1 if the hot acid extraction was used or section 6.3.2 if the ultrasonic extraction procedure was used) to 100 ml with acid of the same concentration as used in preparing the master standard.

9.2 Calibration standards. Prepare daily by diluting the working standard, with the same acid matrix, as indicated below. Other lead concentrations may be used.

Volume of 20 $\mu\text{g/ml}$ working standard, ml	Final volume, ml	Concentration $\mu\text{g Pb/ml}$
0	100	0
1.0	200	0.1
2.0	200	0.2
4.0	100	0.4
8.0	100	0.8
15.0	100	1.6
30.0	100	3.0
50.0	100	6.0
100.0	100	10.0
	100	20.0

9.3 Preparation of calibration curve. Since the working range of analysis will vary depending on which lead line is used and the type of instrument, no one set of instructions for preparation of a calibration curve can be given. Select standards (plus the reagent blank), in the same acid concentration as the samples, to cover the linear absorption range indicated by the instrument manufacturer. Measure the absorbance of the blank and standards as in section 8.0. Repeat until good agreement is obtained between replicates. Plot absorbance (y-axis) versus concentration in  $\mu\text{g Pb/ml}$  (x-axis). Draw (or compute) a straight line through the linear portion of the curve. Do not force the calibration curve through zero. Other calibration procedures may be used.

To determine stability of the calibration curve, remeasure—alternately—one of the following calibration standards for every 10th sample analyzed: Concentration =  $\mu\text{g}$

Pb/ml; concentration  $\pm 10 \mu\text{g Pb/ml}$ . If either standard deviates by more than 5 percent from the value predicted by the calibration curve, recalibrate and repeat the previous 10 analyses.

#### 10. Calculation.

$$C = \frac{(\mu\text{g Pb/ml} \times 100 \text{ ml/strip} \times 12 \text{ strips/filter}) - F_b}{V_{\text{STP}}}$$

where:

C=Concentration,  $\mu\text{g Pb/sm}^3$ .  
 $\mu\text{g Pb/ml}$ =Lead concentration determined from section 8.

100 ml/strip=Total sample volume.

12 strips=Total useable filter area,  $8'' \times 9''$ .  
 Exposed area of one strip,  $\frac{3}{4}'' \times 7''$ .

Filter=Total area of one strip,  $\frac{3}{4}'' \times 8''$ .

$F_b$ =Lead concentration of blank filter,  $\mu\text{g}$ , from section 6.1.1.2.3.

$V_{\text{STP}}$ =Air volume from section 10.2.

#### 11. Quality control

$\frac{3}{4}'' \times 8''$  glass fiber filter strips containing 80 to 2000  $\mu\text{g Pb/strip}$  (as lead salts) and blank strips with zero Pb content should be used to determine if the method—as being used—has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

To minimize the possibility of generating unreliable data, the user should follow practices established for assuring the quality of air pollution data, (13) and take part in EPA's semiannual audit program for lead analyses.

#### 12. Trouble shooting.

1. During extraction of lead by the hot extraction procedure, it is important to keep the sample covered so that corrosion products—formed on fume hood surfaces which may contain lead—are not deposited in the extract.

2. The sample acid concentration should minimize corrosion of the nebulizer. However, different nebulizers may require lower acid concentrations. Lower concentrations can be used provided samples and standards have the same acid concentration.

3. Ashing of particulate samples has been found, by EPA and contractor laboratories, to be unnecessary in lead analyses by atomic absorption. Therefore, this step was omitted from the method.

4. Filtration of extracted samples, to remove particulate matter, was specifically excluded from sample preparation, because

10.1 Measured air volume. Calculate the measured air volume at Standard Temperature and Pressure as described in Reference 10.

10.2 Lead concentration. Calculate lead concentration in the air sample.

some analysts have observed losses of lead due to filtration.

5. If suspended solids should clog the nebulizer during analysis of samples, centrifuge the sample to remove the solids.

#### 13. Authority.

(Secs. 109 and 301(a), Clean Air Act, as amended (42 U.S.C. 7409, 7601(a)))

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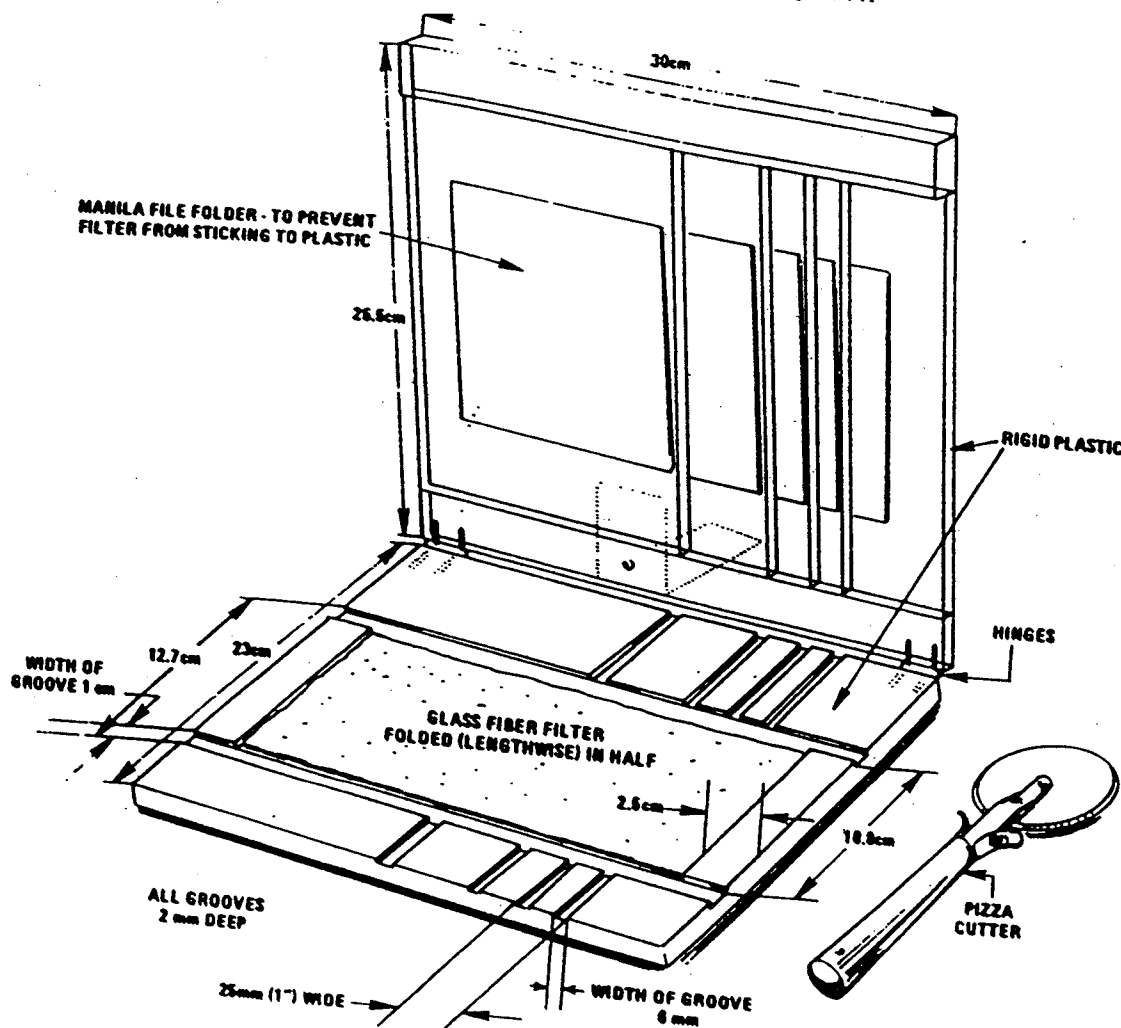


Figure 1

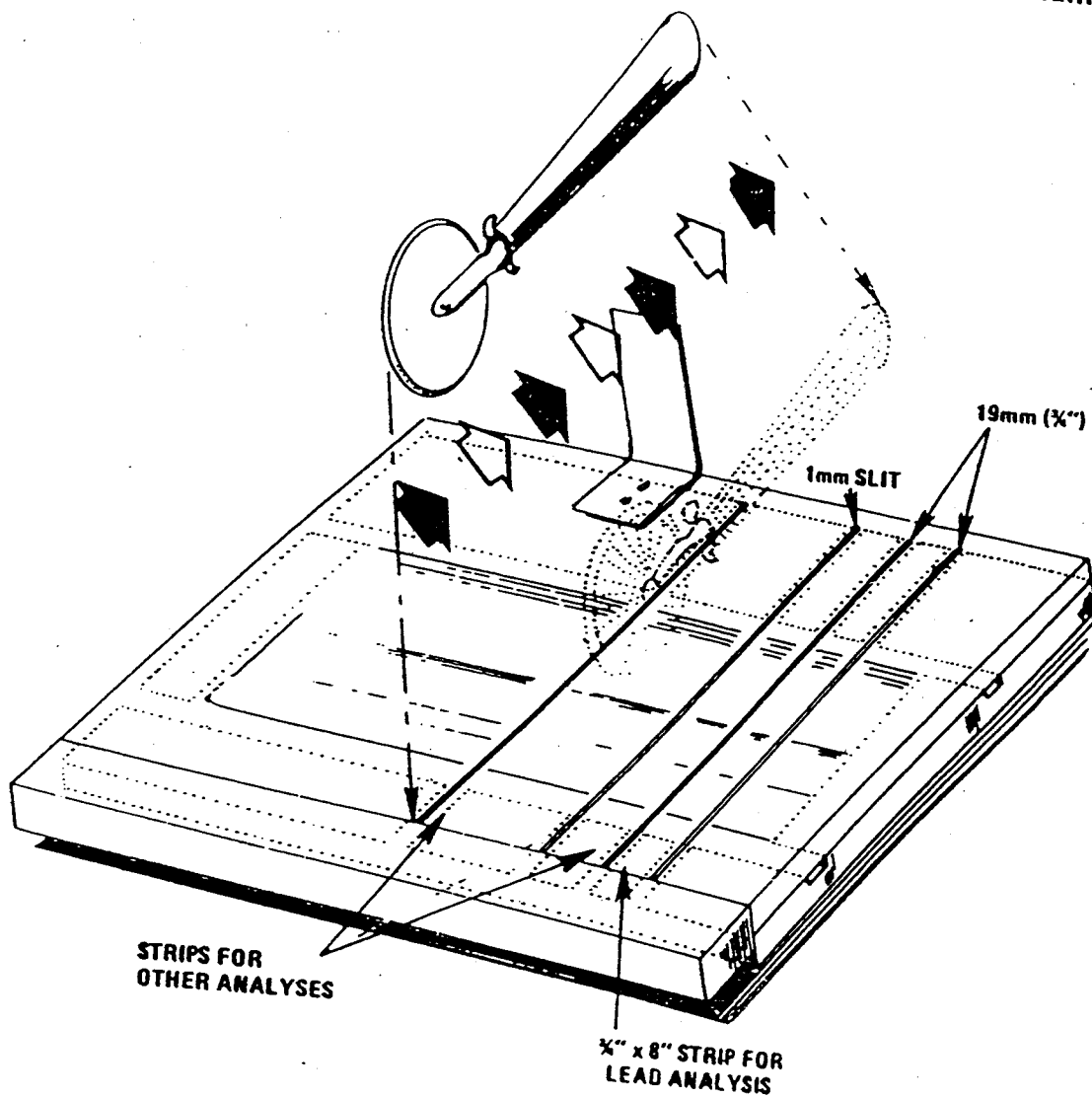


Figure 2

(Secs. 109, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7409, 7601(a)); secs. 110, 301(a) and 319 of the Clean Air Act (42 U.S.C. 7410, 7601(a), 7619))  
 [43 FR 46258, Oct. 5, 1978; 44 FR 37915, June 29, 1979, as amended at 46 FR 44163, Sept. 3, 1981; 52 FR 24664, July 1, 1987]